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ANNUAL CATALYST RESEARCH PROGRAM REPORT

SUMMARY

HEALTH EFFECTS RESEARCH LABORATORY

SEPTEMBER 1975

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Ecological Research Series

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AUTO CATALYST RESEARCH PROGRAM REPORT

Summary

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16. ABSTRACT

This report constitutes the first Annual Report of the ORD Catalyst Research Program required by the Administrator as noted in his testimony before the Senate PUblic Works Committee on November 6, 1973. It includes all research aspects of this broad multi-disciplinary program including: emissions characterization, measurement method development, monitoring, fuels analysis, toxicology, biology, epidemiology, human studies, and unregulated emissions control options. Principal focus is upon catalyst-generated sulfuric acid and noble metal particulate emissions.

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ANNUAL CATALYST RESEARCH PROGRAM REPORT

Summary

by

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U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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CATALYST RESEARCH PROGRAM

ANNUAL REPORT

Office of Research and Development
and
Office of Air and Waste Management

U. S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
National Environmental Research Center
Research Triangle Park, North Carolina

June 1975

EXECUTIVE SUMMARY

EPA Administrator Russell Train's mandate for an accelerated and expanded research program on the mobile source oxidation catalytic converter in late 1973 initiated the development of interdisciplinary examination of the potential public health impact of both regulated and unregulated emissions from catalyst-equipped vehicles by both the Office of Research and Development and the Office of Air and Waste Management. The strategy underlying the establishment of the program can briefly be summarized in the following five objectives:

1. Identify emissions
2. Determine emission factors
3. Estimate human exposure
4. Assess public health impact
5. Evaluate control options
6. Provide timely reports to provide basis for management decisions

Within this framework, the resources available both within EPA and in the research community were marshalled to address the issue. The program areas involved in the effort have been as follows:

1. Emissions characterization
2. Emission measurement methodology development
3. Meteorological modelling
4. Toxicology (classical and inhalation)
5. Human health studies (epidemiology, occupational exposure)
5. Control technology

Each of the above areas of expertise impinges upon one or more of the others; this fact necessitated from the beginning of the program close coordination, clear definition of objectives and methods, and centralized program direction. Since the program cut across traditional

organization structures, a matrix approach emerged as the appropriate management tool for effective use of disparate and diverse resources both human and financial. The specific areas of research completed, current, and planned are treated in this report according to these program areas in identified appendices, but conclusions regarding the implications of the results of these research efforts must and will be evaluated as an integrated body of knowledge.

Summary technical conclusions based upon results of the program to date are as follows:

1. Our current (1974 model year and older) in-use light-duty motor vehicle population emits trace quantities of sulfuric acid.

2. Current ambient sulfate particulate levels reported by epidemiological studies (CHESS) already exceed the estimated health effects threshold many days of the year in many urban centers, particularly in the northeastern United States.

3. Oxidation catalyst-equipped light-duty motor vehicles emit sulfuric acid aerosol. While non-catalyst-equipped vehicles appear to convert about 1% of fuel sulfur to sulfuric acid, catalyst cars convert 20 to 40% of such sulfur to sulfuric acid with air-injected catalyst-equipped vehicles being the higher emitters.

4. Catalyst-generated sulfuric acid aerosol will result in localized incremental exposures to persons on and near major highways and other areas of high motor vehicle density.

5. The catalyst-generated localized incremental sulfuric acid exposures are projected to exceed the estimated health effects threshold 2 years after vehicles have been equipped with catalysts in California and (after 3 to 4 years in the rest of the nation). Such exposures will occur on and near our busiest highways.

6. Development of a reliable analytical measurement method specific to ambient sulfuric acid is crucial, as no specific method now exists The wet chemical techniques for ambient particulate sulfate are not necessarily specific for sulfates; sulfides and sulfites, if present will interfere. Thus, the present techniques measure total particulate water soluble sulfur compounds.

7. Existing (pre-catalyst) baseline data establishing current rural, urban, and occupationally-exposed human burdens of platinum and palladium needs to be clearly defined and are under investigation.

8. Research into long-term health effects of platinum, palladium, and sulfuric acid must be continued.

9. Methods to control sulfuric acid emissions from catalyst-equipped vehicles must be pursued.

10. Preliminary pre-catalyst baseline studies on the Los Angeles freeway monitoring site tend to confirm via CO, Pb, and SO_2 surrogates the projected incremental sulfuric acid exposures.

Policy implications of the above technical conclusions are as follows:

1. Data on ambient and exhaust sulfate levels available thus far suggest that an ambient standard for sulfates be considered.

2. For the same reasons, the feasibility and desirability of controlling motor vehicle emissions of sulfate must also be considered.

3. Resolution must be made between the fact that current suggested threshold health effects levels of sulfates may be exceeded on and near major highways within two years and the fact that the earliest possible date of application of controls for motor vehicle sulfate emissions would very likely be three years hence, at a minimum.

INTRODUCTION

Section 202 of the Clean Air Act of 1970, as amended, mandated substantial reductions in certain specified emission products from automobiles. The automotive industry, to achieve this reduction, chose the oxidation catalytic converter as a primary method of emission control for model year 1975. After this decision was made known to EPA the Agency intensified its research program to determine what, if any, new pollutants might be emitted into the atmosphere as a result of the application of this technology. Also studied were the effects of fuel composition and fuel additives on these, as well as regulated, emissions. The EPA research program results indicated that though emissions of hydrocarbons, carbon monoxide, and certain organics would be dramatically lowered, sulfuric acid aerosol emissions would increase, and slight emissions of platinum, palladium, and alumina might also be expected.

Since existing ambient concentrations of sulfates in many areas of the country have been shown to be at levels sufficient to cause concern to those in EPA and elsewhere responsible for the protection of public health, and since very little information existed regarding health effects of platinum or palladium as air pollutants, EPA initiated a broad research program to examine the questions of public health impact of these three pollutants: catalyst-emitted sulfates, platinum, and palladium.

In testimony to the Public Works Committee of the U. S. Senate, Administrator Train specified EPA's planned program of catalyst-related research:

1. Accelerate work on development of a reliable test procedure for automotive sulfate emission measurement.
2. Consider all feasible alternatives for automotive sulfate emission control.
3. Improve the Agency's ability to estimate the public health impact of sulfate and other automotive emissions.

4. Improve understanding of the atmospheric chemistry involved in these emissions and initiate an appropriate air monitoring program.

From these broad objectives defined in Administrator Train's testimony of November 1973, an extensive interdisciplinary research program utilizing the resources of a broad range of EPA's technical staff both with the Office of Research and Development and the Office of Air and Waste Management and of the scientific community outside the government through extramural programs, was developed. The program has been designated as priority number one in EPA's research effort. This program has now completed its first six months of effort. The results are summarized in the following report, which will be the first of a series to be issued annually through at least 1977.

PROGRAM SUMMARY

The thrust of the catalyst research program is to evaluate the potential public health impact of emissions unique to catalyst-equipped automobiles. The issue is a complex one, requiring the best efforts of scientific and technical staff from several disciplines. Although many other fields of scientific/technical study are tangentially related to the catalyst program, the major program areas involved are as follows:

1. emissions characterization - necessary to determine what specific chemical elements and/or compounds should be studied to assess health effects and whether new or higher levels of pollutants are present

2. emissions measurement methodology development - necessary to assign quantitative numbers to levels of a given pollutant for purposes of comparison, and to assign relative priorities related to projected public exposures

3. meteorological modelling - necessary to project dispersion route of pollutants from the source through ambient air to determine probable areas and levels of exposure resulting from given source emissions

4. toxicology - necessary to determine the risk to health posed by a given substance relative to compounds known to have serious adverse health effects

5. human studies - necessary to determine the effects of chronic or intermittent exposure to substances on human health, both reversible and irreversible, and relative to both the general population and to high risk populations (once identified)

6. control technology - necessary to evaluate the feasibility and effectiveness of means of controlling emissions of pollutants shown to have adverse health or welfare effects

In the catalyst research program, the first program area has been a joint Office of Research and Development and Office of Air and Waste Management effort; the next four program areas have been the responsibility of the Office of Research and Development; the sixth has been that of the Office of Air and Waste Management. In addition to research specifically addressed to the catalyst issue, many continuing programs basic to the Agency's total research effort are related and will be included when appropriate.

Specific research tasks within the ORD catalyst research program are listed below. The currently available information on each such area is discussed in the "technical conclusions" section, and further information is contained within the detailed technical appendices of this report.

TASK DESCRIPTIONS - ORD PROGRAM

ORD Program Element 1AA002, "Fuel and Fuel Additive Registration"

1. Emission Characterization (Appendix B2)

ORD Research Objective Achievement Plan (ROAP) 21BCE -- "Health and welfare impact of catalysts used in the control of mobile sources of air pollutants"

Task

001 Survey and gaseous particulate emissions - California 1975 model year vehicles

002 Characterize particulate emissions, prototype catalyst cars

044 Characterize particulate emissions from production catalyst-equipped cars

045 Operate dynamometer and test equipment in support of catalyst-related emissions method development and characterization studies

046 Procure test and data acquisition equipment in support of catalyst-related emissions testing program

070 In-house and field evaluation of existing analytical sampling and analysis schemes pertinent to the determination of pollutants emanating from catalyst-equipped automobiles

082 Characterization and measurement of regulated, sulfate, and particulate emissions from in-use catalyst vehicles - 1975 national standard

ORD Research Objective Achievement Plan (ROAP) 26AAE -- "Development of information for fuel and fuel additives control or prohibition"

012 Characterize current vehicle gaseous emissions

014 Characterize alternate power systems (rotary)

017 Characterize particulate emissions - alternate power systems (rotary). Develop protocol

018 Characterize detailed gaseous and particulate emissions -- non-catalytic advanced control prototypes

019 Characterize diesel gaseous and particulate emissions

2. Emissions Measurement Methodology (Appendix B3)

ORD Research Objective Achievement Plan (ROAP) 21BCE --
"Health and welfare impact of catalysts used in the control of mobile sources of air pollutants"

Task

004 Develop methodology to determine the effect of gas composition and additives on emissions control device performance

039 Analysis of "unusual" emissions from current and future mobile sources -- impact of control devices

042 Adapt methods for SO_2 and SO_3 to mobile source emissions measurement

043 Develop methods for total sulfur, sulfate, and other sulfur compounds in particulate emissions from mobile sources

056 Standardized methods for measurement of and collection and analysis of particulate sulfates

057 Quality assurance guidelines for measurement methods applicable to mobile sources and fuels and fuel additives

058 Development of standard reference materials for emissions from mobile sources and fuels and fuel additives

059 Collection and analysis of samples at selected sites, including sulfate, trace metals, and nitrates

060 Collection and analysis of samples at selected sites, including sulfate, trace metals, and nitrates

061 Determination of various pollutants in TSP, fine particulate, and soil samples

064 Survey and evaluate analytical methods pertinent to Task 065 and 066

065 Standardized method for measurement of exhaust and ambient sulfates

066 Standardized methods for noble metals and catalyst support materials

067 Develop standard reference materials for mobile source pollutants measurements

068 Conduct interlaboratory performance surveys for sulfate and catalyst-related particulates

070 In-house and field evaluation of existing analytical sampling and analysis schemes pertinent to the determination of pollutants emanating from catalyst-equipped automobiles

3. Fuel Collection and Analysis (Appendix B1)

Research Objective Achievement Plan (ROAP) 21BCE

Task

055 Commercial fuels collection and analysis

062 Maintain national sample bank and implement data acquisition and processing system

063 Expand network for collection and analysis of fuel samples specificially in southern California in support of catalyst field program

4. Toxicology (Appendix B4)

Research Objective Achievement Plan (ROAP) 21BCE

Task

005 Estimate no-effect level using mouse pulmonary infectivity model

(a) of appropriate Pt-group metal compounds administered singly

(b) of base metal compounds administered in appropriate combination

006 Compare relative toxicity against Pb compounds using in vitro macrophage system -- of Pt-group compounds

007 Compare relative toxicity against Pb compounds using in vitro conjunctival cell and respiratory epithelial cell cultures -- of Pt-group compounds

008 Estimate no-effect level of Pt-group metal compounds using immediate and delayed allergic response in animals

009 Compare relative cytogenicity against Pb compounds using in vivo hamster system

(a) of Pt-group compounds

(b) of base metal compounds

010 Compare relative mutagenicity of Pb compounds using host-mediated assay system

011 Compare relative toxicities against Pb compounds using biochemical parameters

(a) of Pt-group compounds

(b) of base metal compounds

012 Compare pulmonary carcinogenicity of Pt-group metal compounds and of Pb compounds in association with polynuclear armoatics using in vivo hamster system

022 Comparative methylation chemistry of Pt-group compounds, selected base metals, and lead with subsequent toxicological assessment of stable metallic compounds

025 Analysis of animal tissues for platinum, palladium, lead, and manganese

074 Toxicology of respirable sulfur compounds

075 Toxicological evaluation of airborne respirable particulates and mists

5. Inhalation Toxicology (Appendix B5)

ORD Program Element 1AA007

Research Objective Achievement Plan (ROAP) 21AFK

Office of Research and Development
National Environmental Research Center
Environmental Toxicology Laboratory
Cincinnati, Ohio

ORD Program Element 1AA002

Research Objective Achievement Plan (ROAP) 21BCE

Task

013 Toxicological evaluation of whole engine exhausts from catalytic-controlled systems

076 Comparative inhalation toxicology specific to catalyst nonregulated emissions

077 Long-term, low-level comparative inhalation toxicology specific to nonregulated emissions from oxidation catalysts

6. Meteorology (Appendix B6)

Research Objective Achievement Plan (ROAP) 21BCE

Task

027 Validation of highway gaseous dispersion model for simulation of air quality

028 Conduct wind tunnel experiments to evaluate current highway model for gaseous emissions. Monitor Tasks 029/030 -- prepare reports

029 Evaluate applicability of highway gaseous dispersion model for mobile source particulate and aerosol species

030 Develop and evaluate dispersion model for complex mobile sources

7. Atmospheric Chemistry (Appendix B7)

Research Objective Achievement Plan (ROAP) 21BCE

Task

003 Visibility effects of catalyst and non-catalyst advanced prototype vehicles

040 Atmospheric chemistry of acid aerosols

041 Personal exposure meters for suspended sulfates

048 Particle size, chemical characterization, formation, and growth roles of scattering roadside aerosols

049 Study of scavenging of SO_2 and sulfates by surfaces near roadways

050 Smog chamber study of SO_2 photo-oxidation to SO_4 under roadway conditions

052 Develop portable device for collection of sulfate and sulfuric acid

053 Develop laboratory method for collected sulfate and sulfuric acid aerosols

054 Fabricate 12 portable samplers for measurement of sulfuric acid

079 Characterization of roadside aerosols for St. Louis. Particle size, chemical composition, formation, growth, and light scattering of roadside aerosols

8. Monitoring (Appendix B8)

Research Objective Achievement Plan (ROAP) 21BCE

Task

024 Monitor air quality along a major highway in southern California. Utilizing existing methods, analyze water-soluble sulfate, lead, and TSP at 4 sites and CO at 1 or 2 sites. Additionally, 1 meteorology station will be established and total motor vehicle count (not vehicle mix) at 1 site will be made (4-month task). (FY 74)

071 Same as Task 069 with the addition of traffic mix data, TSP, size distribution at one station, one or two additional hi-vols at a distance away from the highway, and of TSP samples. (Pt methodology is not fully developed, coordination needed with CPL). (3-year study)

072 Handling, validating, and interpreting data from southern California, and complex source studies, including report writing and computer costs

073 Monitor complex sources such as street canyons, shopping centers, and parking garage in southern California for mobile source pollutants (FY 76)

080 Assist in sampling and analysis for Los Angeles Catalyst Study (LACS). (Task 071)

9. Human Studies (Appendix B9)

Research Objective Achievement Plan (ROAP) 21BCE

Task

014 Effects of chronic or intermittent exposure to low levels of major catalyst attrition products or their decay products on human pollutant burdens

015 Effects of above (14) on irritation symptoms in humans

016 Assessment of subtle physiologic changes induced by exposure to major catalyst attrition products or their decay products, enzyme changes, immunologic deficits, chromosomal abberations, etc.

031 Public health impact of suspended particulate sulfates

032 Public health impact of suspended particulate sulfates

033 Analysis of tissue samples collected throughout CHESS network to assess population pollutant burdens of Pt, Pd, and Al

034 Clinical studies of human response to noble metals

035 Effects of controlled exposure to specific particulate pollutants on immune response

036 Effect of particulate sulfates and noble metals on human behavior

037 Effects of ambient exposure to selected chemical particulates on the occurrence of carcinogenic or mutagenic effects

038 Comprehensive PFT on high risk population

081 Development of sensitive biochemical and behavioral indicators of trace substance exposure

10. Control Technology (Appendix A)

Office of Air and Waste Management

TECHNICAL CONCLUSIONS

This first annual research report contains information on research programs principally initiated during the current fiscal year. Thus, the technical conclusions reviewed herein are largely based upon preliminary data. Based upon these studies, the following conclusions have been drawn:

1. Two collection methods have been employed by EPA and industry laboratories in effort to ascertain the emission rate of sulfuric acid from non-catalyst and catalyst-equipped vehicles. Data derived from the application of the stationary source Method 8 technique suggested that sulfuric acid was emitted from both non-catalyst- and catalyst-equipped vehicles. The air-diluted particulate method suggested that only trace amounts of sulfuric acid was emitted from non-catalyst vehicles, while significant quantities were emitted from catalyst-equipped vehicles. The Method 8 technique has now been shown to generate artifact sulfate. We now believe that only the air-diluted particulate collection procedures provide valid sulfuric acid collection from mobile sources.

2. Current data indicate that non-catalyst-equipped vehicles emit only trace quantities of sulfuric acid whether equipped with air pumps or not.

3. Catalyst-equipped vehicles do convert some of the fuel sulfur combusted to sulfuric acid which is emitted in a fine aerosol form. The earlier EPA emission factor estimate of 0.05 gm/mile sulfuric acid for a fuel containing 300 ppm sulfur is now felt to be approximately correct. However, certain catalyst types make a precise estimate of the emissions factor very difficult due to severe sulfate

storage and release phenomena, making estimates based upon emission rates from catalyst-equipped vehicles operated on the Federal Test Procedures unreliable.

4. The Federal Test Procedure (CVS-75) cannot be used as a basis for determining sulfuric acid emission rates from catalyst-equipped vehicles due to catalyst sulfate storage problems. Work is under way to attempt to derive an appropriate test cycle to permit correlation of sulfuric acid emissions with localized air quality exposure projections.

5. Sulfuric acid emission rates from oxidation catalyst-equipped vehicles are dependent not only upon catalyst type, as noted in 3 and 4 above, but also upon fuel sulfur levels, fuel economy, mode of vehicle operation, catalyst preconditioning, and catalyst age. These factors compound the researcher's problem in attempting to derive a meaningful emission factor.

6. An automated method has been developed and tested for the determination of sulfuric acid concentrations from the exhaust air-diluted particulate collection procedure. A multi-laboratory analysis round-robin is currently under way to ascertain the reproducibility of the sulfuric acid measurement techniques. The method appears to be highly reliable, reproducible, and accurate. The methods (air-dilution collection and automated SO_4 method) have been installed and are operating in the OAWM Ann Arbor emissions laboratory.

7. The use of oxidation catalysts on motor vehicles results in a substantial decrease in the emissions of carbon monoxide, unburned hydrocarbons, phenols, aldehydes, polynuclear aromatic hydrocarbons, and organic particulates. This is a positive public health benefit.

8. Several sulfuric acid emission control techniques are under investigation. Fuel desulfurization is one such approach which will, of course, reduce such emissions. Preliminary technical feasibility, cost, timing, and impact studies have been completed. Other approaches being pursued include a sulfate emission standard, a particulate emission standard, potential low-sulfate emission catalyst systems, and sulfate traps.

9. While earlier work with pre-production catalysts indicated that some of the catalyst substrate and active components (platinum and palladium) were emitted as particulate, recent studies by EPA and industry laboratories with production catalysts suggest that such emissions are at extremely low levels. What, if any, such emissions occur during or after catalyst poisoning or thermal failure is not, however, known at this time.

10. Insufficient information is available to assure that the public health will not be adversely affected by the platinum and palladium used in current oxidation catalysts. While studies to determine living human burdens of these metals in urban and rural settings are nearing completion, occupationally exposed persons have not been examined as yet. The available toxicological, biological, and human data suggests that the public health will likely <u>not</u> be adversely affected

by the introduction of noble metal catalysts in the short term. Long range chronic studies are, of course, not completed nor are the methylation chemistry studies currently under way.

11. Emission data and baseline pre-catalyst datalyst data from the Los Angeles area freeway monitoring site suggest that the earlier projections presented in the Agency technical papers on the subject to the Senate Public Works Committee on January 11, 1974, are valid. That is, incremental localized exposures to sulfuric acid generated from catalyst-equipped vehicles will exceed the estimated health effects threshold several days per year on our busiest freeways after two model years of vehicles are equipped with such devices. These projections assume that 25% of the vehicles miles are driven with catalyst-equipped vehicles. Because all 1975 vehicles are not equipped with catalysts, with the exception of California, and due to the fact that the '75 interim emissions standards will be in effect through model year 1976, at least, these projections appear valid for California only. We, therefore, expect that major urban centers outside California would not experience these incremental exposure levels for at least three years. Decreased sales of new motor vehicles at levels less than recent years, increased purchases of vehicles with improved fuel economy, and decreased vehicle miles driven would all tend to stretch out the time required to generate adverse incremental exposures.

12. Current ambient sulfate levels already exceed the estimated health effects threshold many days of the year in our major Northeastern urban centers.

13. No proven measurement method now exists to permit the accurate analysis of sulfuric acid aerosols in ambient air. Work to develop such techniques is being vigorously pursued.

Discussion

This first annual research report on EPA's catalyst emissions research program is intended to provide both an overview, with preliminary conclusions, and the details of the research information currently available from the program. This report will be updated on an annual basis. It is our intention that this report provide a brief overview of the program and the conclusions. The technical appendices provide an in-depth view of the many individual research efforts which comprise the total program.

Over 2 years ago, it was first recognized by a contractor to EPA that particulate emissions from catalyst-equipped vehicles operating on lead-free fuel were substantially higher than from non-catalyst vehicles operating on the unleaded fuel. The contractor, in cooperation with Ford Motor Company scientists, identified the bulk of the additional particulate generated as sulfuric acid. These findings prompted the EPA laboratories in Ann Arbor, Michigan and Research Triangle Park, North Carolina to expand their programs to assess non-regulated emissions from oxidation catalyst-equipped prototype vehicles. At about the same time, Esso Research and Engineering (now Exxon Research and Engineering) reported similar findings to EPA.

The initial efforts of these various investigations were reported in hearings before the Committee on Public Works of the U.S. Senate on November 5 and 6, 1973.[1] The Administrator testified before the Committee (page 431, Ref. 1) on November 6, 1973. His decision regarding the use of catalysts on 1975 model year vehicles was based upon three technical papers prepared by EPA and formally forwarded to the Senate on January 11, 1974.[2] That decision is best summarized from testimony:

"I intend to make no change in the emission standards that are currently promulgated to be applicable to the 1975 model year, and to take no action that would inhibit the use of catalysts on 1975 cars. At the same time, however, EPA will do the following:

1. Accelerate our work on developing a test procedure of assured reliability for measuring emissions of sulfates from cars;
2. Consider all feasible measures for controlling sulfate emissions from cars, including a regulatory approach to controlling sulfur content in gasoline and other alternatives. In the next few weeks, EPA intends to begin a process of soliciting the views of all interested parties. EPA will then be in a position to initiate a regulatory proposal, if studies indicate such action is necessary to protect public health. In addition, we intend to encourage the petroleum industry to voluntarily make available unleaded gasoline of low sulfur content for the 1975 model vehicles;
3. Improve our ability to estimate the impact of sulfate and other emissions from cars on air quality and public health; and
4. Improve our understanding of the atmospheric chemistry involved and institute an appropriate air monitoring program."

The material covered by this first annual catalyst research program report is responsive to the mandate established by Administrator Train as outlined in items one through four of this testimony as quoted above. Subsequent discussion will address each item.

"1. Accelerate our work on developing a test procedure of assured reliability for measuring emissions of sulfates from cars;"

At the time EPA was preparing testimony for the Senate regarding catalyst-generated sulfuric acid, two rather different approaches were being used to ascertain the emission levels of sulfuric acid. One, an

adaption of a stationary source SO_2/SO_3 method (referred to as Method 8) was principally used by the EPA laboratory in Ann Arbor and by Chrysler Corporation. Data obtained by this method indicated that sulfuric acid was emitted by non-catalyst vehicles while catalyst-equipped vehicles emitted substantially higher levels.[2] The other method, used in minor variations of design was an exhaust-air diluted particulate technique pioneered by Habibi.[3] This method indicated that little or no sulfuric acid was emitted by non-catalyst vehicles but that easily measurable quantities were emitted by oxidation catalyst-equipped vehicles. At the time the Administrator made his decision regarding the use of catalysts on 1975 vehicles, it was not known which method was correct.

The Office of Research and Development in the National Environmental Research Center, Research Triangle Park, N.C., has devoted considerable effort during the past year to examining the question of a reliable and accurate sulfuric acid measurement method. We have concluded that the stationary source Method 8 results in "artifact" sulfate (Appendix B3.4). Further, the exhaust-air dilution technique provides a highly reliable, repeatable, and accurate method for ascertairing sulfuric acid emissions from motor vehicles (Appendix B2.2, B3.7, B3 8) (The exhaust-air dilution method has subsequently been installed in the Ann Arbor facility.). We, therefore, conclude that current vehicles, whether equipped with air pumps or not, emit trace quantities of sulfuric acid.

The emission rate of sulfuric acid from oxidation catalyst-equipped vehicles, while clearly established, is somewhat more difficult to quantify. Sulfuric acid emissions are dependent upon at least the following variables: vehicle cycle, catalyst type, fuel sulfur level, catalyst age, degree of HC/CO control desired (75 National Interim Standard vs 75 California Interim Standard), fuel economy, catalyst pre-conditioning, catalyst operating temperature, and catalyst volumetric flow rate. Major determinants are known to be fuel sulfur levels, vehicle cycle, and catalyst type.

Increased fuel sulfur levels do result in increased sulfuric acid emission levels. Cold start Federal Emissions test procedures result in lower sulfuric acid emission rates than do cruise modes. The monolithic type catalysts exhibit much higher sulfuric acid emission rates during the cold start FTP than do the beaded catalyst systems. The beaded systems, however, exhibit very high transient sulfuric acid emissions when operated from the FTP to a cruise mode. This phenomenon is due to the fact that the beaded catalyst system stores large quantities of sulfur compounds during cold operation and releases them as both SO_2 and sulfuric acid when operated under the higher temperatures associated with cruise operation. At the present time, it appears that both systems emit about the same amount of sulfuric acid when the urban cold-start (FTP) cycle, transient, and cruise modes are considered.

Other data suggest that catalyst age, catalyst pre-conditioning (particularly for beaded systems), catalyst operating temperature, and exhaust flow rate through the catalyst are also minor determinants of sulfuric acid emission rates. As with fuel sulfur level, the fuel economy of the specific vehicle being evaluated is an important factor in determining the sulfuric acid emission rate.

Limited data with 1975 production vehicles indicate that those achieving the more stringent 197 alifornia emissions standards also emit higher levels of sulfuric acid. This will be better quantified in the near future.

We have reviewed the factors which affect the generation and collection methods for exhaust sulfuric acid. The third critical area in assessing sulfuric acid emission rates is the analysis of the collected particulate sample. Various investigators have used several techniques. ORD at NERC/RTP has developed a highly accurate automated barium method (Appendix B3.6). The method, in this laboratory, has been compared to the

Thorin method, x-ray fluorescence, and atomic absorbtion techniques while utilizing a variety of particulate collection media. The automated barium method has been shown to be highly reliable, accurate, and repeatable, particularly for samples collected on fluoropore filter media and is superior to the other methods examined. This method is also now being used in the Ann Arbor laboratory and in a number of industry laboratories. In addition, a number of laboratories are currently involved in a round-robin sulfate analysis method comparison study which involves a multi-laboratory analysis of a large batch of particulate from a catalyst vehicle collected at the RTP laboratories. The results of this study should be available within a few months.

In summary, we now can conclude that non-catalyst vehicles emit little, if any, sulfuric acid; that catalyst cars do emit sulfuric acid; and while we now have reliable collection and analysis techniques for mobile source generated sulfuric acid, we also are more fully aware of they many factors which are important in determining the sulfuric acid emission rate. At this time, we believe that the emission factor estimate (.05 gm/mile) used in the Agency's technical papers in support of the Administrator's Senate testimony is approximately correct.

The final aspect of our program to determine emission rates of sulfuric acid from catalyst-equipped vehicles involves two in-use consumer-owned, operated, and maintained vehicle studies. All current data have been obtained in the laboratory using prototype, pre-production, and a small number of production 1975 catalyst-equipped vehicles. It is the intent of the two field programs to obtain data on the emissions of regulated pollutants (CO, HC, NO_x) and selected non-regulated pollutants (particulates and sulfates) from 1975 California standard vehicles and from 1975 National standard vehicles. Emission factors for these pollutants from a fairly large number of vehicles owned, operated, and maintained by the consuming public and using commercial fuels

purchased by the public will provide information pertinent not only to the sulfuric acid emission issue but will also provide an index to the reliability of catalyst technology for emissions control (See Appendix B2.5 and B2.6).

"2. Consider all feasible alternatives for controlling sulfate emissions from cars..."

A number of projects have been instituted to evaluate means of controlling sulfate emissions from catalyst-equipped vehicles. This area is the principal responsibility of EPA's Office of Air and Waste Management (OAWM). An extensive cooperative effort exists between OAWM and the ORD emissions research groups in this particular phase of the catalyst program. Options being pursued are:

1. Gasoline de-sulfurization
2. Sulfate traps
3. Minimize sulfate emission by control system modification
4. A mobile source sulfate emission standard

The de-sulfurization program is under the direction of the Office of Air Quality Planning and Standards, OAWM. In November 1973, ORD, NERC/RTP initiated a three-phase study with M.W. Kellogg to ascertain the feasibility, cost, and time required to de-sulfurize gasoline. Appendix A2 contains details of the current status of the de-sulfurization program including the Kellogg reports (A2.2). We can conclude at this time the following regarding the gasoline de-sulfurization option:

1. De-sulfurization of gasoline is technically feasible.
2. De-sulfurization of the special gasoline for catalyst-equipped vehicles to levels of 60 to 100 ppm sulfur (current national average is about 300 ppm) would require an industry capital investment of about $2 to $4 billion.

3. The added cost to the consumer would be around 1¢/gallon.
4. It would require 3-5 years for complete installation of the equipment.

Some discussions have been held between EPA and the Federal Energy Administration regarding the feasibility of allocating low-sulfur crude or finished product to those urban areas which would be most impacted by catalyst-generated sulfuric acid. Such discussions are in the preliminary stage at this time. Aspects of voluntary petroleum industry efforts to provide low-sulfur gasoline for catalyst-equipped vehicles is discussed in Appendix A2.1. In general, some refineries could operationally do so, while others could not without equipment investment. A recent survey of sulfur levels in the unleaded gasoline grade, while limited, shows values ranging from 25 ppm to over 900 ppm sulfur. One might expect this range to narrow as the demand for the unleaded grade increases with increasing 1975 vehicle purchases.

Sulfate traps and the catalyst operating conditions study are covered in detail in Appendix A1. The catalyst operating conditions study is principally directed at ascertaining the critical parameters of catalyst operation which affect sulfuric acid formation. The objective is to define a catalyst type which when operated under select conditions would minimize the SO_2 conversion to sulfuric acid and yet provide the HC and CO control required to achieve the mandated emissions standards. At this time, a number of sulfuric acid determinants have been identified, most of which have been reviewed earlier in this discussion.

Sulfate traps, and from a regulatory point of view, a sulfate emission standard for new motor vehicles are also being actively evaluated. The results to date are summarized in detail in Appendix A1, as noted earlier. While the program is in preliminary stages, the sulfate trap approach appears to be cautiously optimistic. Implementation of such

traps would likely hinge upon regulatory standards limiting sulfuric acid emissions from new light-duty motor vehicles by EPA. Such standards would require three years for implementation at a minimum.

In March 1974, EPA published, in the Federal Register, a notice seeking information from interested parties on the catalyst sulfuric acid issue. Many responses were received. These have been reviewed and discussions pertinent to the various aspects of the issue were prepared by an OAWM-ORD task force. The responses and EPA's analysis thereof will be available in the near future from OAWM. In summary, the responses provided little new information that would assist the Agency in evaluating the potential public health impact of the use of oxidation catalysts on light-duty motor vehicles beyond that being obtained from the program being reviewed in this report.

"3. Improve our ability to estimate the impact of sulfate and other emissions from cars on air quality and public health;"

When the emission factor of a new pollutant has been determined, the next two critical steps in assessing impact involve estimating exposure levels and ascertaining whether such levels pose a threat to public health. In the case of sulfuric acid and catalyst attrition products, a number of approaches to estimating exposure levels were noted, but the principal technique involved application of meteorological highway models.[2] Once preliminary exposure estimates were completed, potential adverse health effects were estimated, based, in part, upon the extensive atmospheric sulfate background information available from the Office of Research and Development Community Health and Environmental Surveillance System (CHESS). Assessment of potential public health risk due to catalyst attrition products was quite another issue, as little information was available within EPA or the technical literature. As a result, substantial toxicological, biological, and human studies were initiated.

Of equal importance was the assessment of the public health benefits associated with reduced emission levels of regulated motor vehicle pollutants, i.e., CO, oxidants (HC), and NO_x.

Exposure estimates have relied principally upon the application of highway CO dispersion models (Appendix B6.2). Subsequent to the EPA technical paper submitted to the Senate on this subject,[2] these models have been further evaluated and are presented in Appendix B6.3. Contained within B6.3 is an example of line source CO dispersion modelling which relates to the catalyst sulfate issue. Of particular interest is the graphical presentation relating peak hourly concentration at various receptor distances to the 24-hour average exposure value. It is not, however, known that a dispersion model for a stable gas (CO) is directly applicable to the sulfuric aerosol which is emitted. Studies are under way to assess the relevance of this particular issue.

A number of other methods have been used to estimate exposures. These include CAMP CO monitoring data, Pb surrogates, a CO activity model and a carboxyhemoglobin (COHb) model[1] which is independent of an assumed activity pattern. All such approaches to estimating sulfuric acid exposures have resulted in incremental exposure values of roughly the same magnitude. We, therefore, conclude that such estimates are likely to predict actual exposures. Tables 1 and 2 summarize all currently available exposure estimates. It is important to note however, that all such exposure estimates have been calculated assuming 25% of the vehicle miles travelled are with catalyst-equipped vehicles (2 model years) and that such vehicles emit an average of 0.05 gms/mile sulfuric acid.

Further, it is apparent from Appendix B6.2, B6.3, and Reference 2, that such exposures are localized on and near major sources of vehicular traffic and do not include current ambient background sulfate levels. Also, complex source models (shopping centers, parking garages, etc.) have not been developed. Such models will be developed as part of this program in FY 76.

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[1] See Appendices B6.2, B6.3, and Reference 2.

A fuller discussion of the impact of catalyst-generated localized sulfuric acid on urban commuters in areas with currently existing worrisome ambient sulfate levels is contained within References 4, 5, and 6. Reference 4 also addresses the issue of the benefits associated with regulated emissions reductions from motor vehicles utilizing dispersion model estimates. Table 3 summarizes those findings, while Reference 7 examines such public health benefit aspects from the perspective of the impact of removal of lead from gasoline. Assessment of the potential public health impact of localized exposures to sulfuric acid aerosol generated from catalyst-equipped vehicles has relied heavily upon the ambient sulfate epidemiological studies conducted over the past 3 years by EPA at NERC/RTP. Appendix B9.1 provides the latest update on such studies. Such health assessments including other studies have also been treated in some detail in References 1, 2, 5, 6, 7, 10, and 11. In general, these studies indicate that:

1. There exist within our population people who are particularly susceptible to particulate sulfate exposure. These are those with pre-existing heart and respiratory diseases. Such people comprise approximately 10% of the U.S. population.

2. Susceptible people are believed to exhibit aggravation of symptoms when exposed to levels of approximately 10 $\mu gm/m^3$ of ambient particulate sulfates for a 24-hour period.

3. Ambient sulfates, as measured in these studies, include all water-soluble particulate sulfate species of which sulfuric acid could be one.

4. Sulfuric acid may or may not be a major component of most urban ambient sulfates.

5. Sulfuric acid is likely to be more irritating than the current ambient sulfates at the same concentrations.

While definitive data are lacking, limited human studies[12,13,14] indicate that sulfuric acid should increase pulmonary flow resistance in humans. Morando[15] briefly (15 minutes) exposed young healthy human subjects not accustomed to inhaling H_2SO_4 to concentrations varying from 0.35 to 5.0 mg/m^3. Even at concentrations not subjectively detected by the volunteers (less than 0.05 to 0.7 mg/m^3) the respiratory rate increased rapidly and remained elevated for several minutes after exposure. Amdur[12] observed a respiration rate increase of 30%, inspiration and expiration decreases of 20% and total tidal volume increases of about 28% using human volunteers exposed for 15 minutes to H_2SO_4 levels between 0.35 and 0.5 mgm/m^3.

In human volunteers exposed to H_2SO_4 mist levels greater than 0.35 to 0.5 mg/m^3, bronchiospasm, increased upper respiratory-tract secretions, and a rapid respiration rate were consistently found, along with elevated pulmonary air-flow resistance. All subjects were healthy young adults who could easily compensate for the increased resistance imposed on their breathing. Elevated airway resistance severely hampers breathing in individuals already burdened by cardiorespiratory deficiencies, however, making it more difficult to obtain needed oxygen.

Studies of atmospheric chemistry have shown that at least a portion of the sulfur dioxide (SO_2) emitted to the atmosphere undergoes transformation (oxidation) leading eventually to the formation of sulfuric acid and sulfate particles. Such atmospheric reactions are believed to proceed at a rate from 2 to 15% per hour. Epidemiological, human volunteer, and animal studies demonstrate that some of these oxidized sulfur aerosols and particulates have a much greater irritant potential than sulfur oxide itself. One such aerosol product, sulfuric acid, has been specifically shown to be substantially more irrtating than sulfur dioxide.[15]

Table 1

Incremental Sulfuric Acid Exposure Estimates Summary -- Vehicle Passenger
(25% VMT, All Assuming 0.05 gm/mile H_2SO_4 Emission Rate)

Model	Summary - Including EPA[1] Estimates Incremental H_2SO_4 Exposure Estimates - All Reports	
CO Dispersion	Adverse meteorology - 24-hour average Typical meteorology - peak hourly Adverse meteorology - peak hourly	6.6 - 25.4 $\mu g/m^3$ 7 $\mu g/m^3$ 124 $\mu g/m^3$
CAMP CO	Adverse meteorology - 24-hour average	5.0 - 5.3 $\mu g/m^3$
Pb Surrogate	All - yearly average - 24-hour ranges	1.0 - 5.0 $\mu gm/^3$
CO Activity Model	All - yearly average - 24-hour ranges - living near expressways All - yearly average - 24-hour ranges - living away from expressways	0.6 - 8.8 $\mu g/m^3$ 0.4 - 6.7 $\mu g/m^3$
COHb Model	All - yearly average - 24-hour ranges - urban All - yearly average - 24-hour ranges - suburban	1.6 - 8.1 $\mu g/m^3$ 1.0 - 5.1 $\mu g/m^3$
	EPA projections[1] only	
CO Dispersion	Adverse meteorology - 24-hour average Typical meteorology - peak hourly Adverse meteorology - peak hourly	14.5 $\mu g/m^3$ 7 $\mu g/m^3$ 124 $\mu g/m^3$
CAMP CO	Adverse meteorology - 24-hour average	5.3 $\mu g/m^3$
Pb Surrogate	All - yearly average - peak hourly	3.8 - 5.3 $\mu g/m^3$
CO Activity	All - yearly average - peak hourly	3.8 - 5.3 $\mu g/m^3$
COHb Model	All - yearly average - peak hourly Typical - median day Adverse - worst 2-3 days of the year	3.8 - 5.3 $\mu g/m^3$

TABLE 2

INCREMENTAL EXPOSURE ESTIMATES - AUTOMOTIVE-GENERATED SULFURIC ACID AEROSOL
(25% Vehicle Miles with Oxidation Catalysts. Data Based upon an Emission Rate of 0.05 gm/mile H_2SO_4)

Comparisons of Various Estimates (corrected for emission rate only)				
Exposure Model	Estimate Source	Exposure Estimate	Meteorological Conditions	Receptor
CO Dispersion	EPA	7 $\mu g/m^3$ - peak	Typical	Vehicle passenger
	EPA	124 $\mu g/m^3$ - peak	Adverse	Vehicle passenger
	EPA	5 $\mu g/m^3$ - peak	Typical	10M from roadway
	EPA	88 $\mu g/m^3$ - peak	Adverse	10M from roadway
	EPA	14.5 $\mu g/m^3$ - 24-hr	Adverse	Vehicle passenger
	EPA	11.1 $\mu g/m^3$ - 24-hr	Adverse	10M from roadway
	GM	25.4 $\mu g/m^3$ - 24-hr	Adverse	1M from roadway
		14.7 $\mu g/m^3$ - 24-hr	Adverse	10M from roadway
		6.9 $\mu g/m^3$ - 24-hr	Adverse	50M from roadway
		4.4 $\mu g/m^3$ - 24-hr	Adverse	100M from roadway
		1.1 $\mu g/m^3$ - 24-hr	Adverse	500M from roadway
		6.6 $\mu g/m^3$ - 24-hr	Adverse	1M from roadway
		5 $\mu g/m^3$ - 24-hr	Adverse	10M from roadway
		2 $\mu g/m^3$ - 24-hr	Adverse	50M from roadway
		1.3 $\mu g/m^3$ - 24-hr	Adverse	100M from roadway
		.93 $\mu g/m^3$ - 24-hr	Adverse	500M from roadway
		11.6 $\mu g/m^3$ - 24-hr	Adverse	1M - street canyon
		5.9 $\mu g/m^3$ - 24-hr	Adverse	10M - street canyon
CAMP Station (Chicago) CO Surrogate (not a highway CO value)	EPA	5.3 $\mu g/m^3$ - 24-hr	Maximum CO	
		7.0 $\mu g/m^3$ - 8-hr	Maximum CO	
		9.4 $\mu g/m^3$ - pk-hr	Maximum CO	
	GM	5.0 $\mu g/m^3$ - 24-hr	Maximum CO	
Pb Surrogate	EPA	3.8 - 5.3 $\mu g/m^3$ - pk-hr	All	Vehicle passenger
		3.3 - 6.8 $\mu g/m^3$ - pk-hr	All	Pedestrian
		1.7 - 9.2 $\mu g/m^3$ - pk-hr	All	Urban shopping center
	Ford	1 $\mu g/m^3$ - Av.yr. 24-hr	All	On/Near highway
		3 $\mu g/m^3$ -2-3-hr	Typical	On/Near highway
		5 $\mu g/m^3$ -2-3-hr	Adverse	On/Near highway
	GM	5 $\mu g/m^3$ - 24-hr	Adverse	On/Near highway
Activity Models	EPA			
CO Model		8.8 $\mu g/m^3$ - 24-hr	Adverse	Person living near expressway
		1.3 $\mu g/m^3$ - 24-hr	Typical	Person living near expressway
		6.7 $\mu g/m^3$ - 24-hr	Adverse	Person living away from expressway
		1.0 $\mu g/m^3$ - 24-h4	Typical	Person living away from expressway
		0.6 - 8.8 $\mu g/m^3$ - 24-hr	All	Person living near expressway
		0.4 - 6.7 $\mu g/m^3$ - 24-hr	All	Person living away from expressway
COHb Model		1.6 - 8.1 $\mu g/m^3$ - 24-hr	All	High estimate (urban)
		1.0 - 5.1 $\mu g/m^3$ - 24-hr	All	Low estimate (suburban)

Typical - median day
Adverse - worst 2-3 days of the year

While there are those who are critical of the CHESS epidemiological program, there is sufficient evidence at the present time to consider suspended sulfates as potentially injurious to human health. This requires us to undertake a concerted research effort to define more precisely the adverse health aspects of suspended sulfates and sulfuric acid on human health, particularly in regard to potentiation or aggravation of difficulties already experienced by persons presently burdened by cardiorespiratory deficiencies. It must also be pointed out that the threshold adverse health effects levels estimated for ambient sulfates provide no safety factor for these susceptible groups in our population.

Reference 15 provides an excellent review of several animal studies where exposure to H_2SO_4 aerosol was at least one parameter. That report suggests that laboratory animals have increasing sensitivity to H_2SO_4 aerosols as follows:

Rabbits	-	Least sensitive
Rats	-	↓
Mice	-	↓
Guinea Pigs	-	Most sensitive

A number of conclusions presented in Reference 15 regarding toxicity in experimental animals are highlighted below:

1. Sulfuric acid is a respiratory irritant and can cause death if present in sufficient concentrations.
2. Sulfuric acid causes pathological lesions in the lungs after much less than lethal exposure.
3. Effective, short-term exposures produce a degree of lung damage related to the arithmetic product of concentration and time rather than the concentration alone.
4. Sulfuric acid-induced lung damage is slow to repair.
5. Sulfuric acid aerosol size is an important factor in determining its irritant potency. In long-term studies the effect of 0.9 μ particles was greater than either 0.6 or 9.0 μ particles.

6. Data on mass concentration alone provide an insufficient basis for predicting potency.

7. The particulate oxidation products of sulfur dioxide generally have much greater irritant potency than the parent sulfur dioxide gas.

This review report[15] discussed effects in laboratory animals at many exposure levels of H_2SO_4 alone and in combination with other gaseous and particulate sulfur compounds. Additional work relating to animal exposures to sulfuric acid is contained within Appendices B4.2, B4.3, and B4.4. Detectable lung changes have been identified within these studies at levels as low as 30 $\mu gm/m^3$ (.03 mgm/m^3). These studies are continuing.

Inhalation toxicological studies of exhaust untreated and treated with an oxidation catalyst have been under way at the Environmental Toxicology Research Laboratory, NERC, Cincinnati. Extensive details of this program are contained within Appendix B5.1. This program to date has principally addressed issues related to the benefits associated with catalytic treatment of exhaust pollutants. More specific studies related to sulfuric acid exposures are now under way, utilizing the more sensitive animals (guinea pigs) and longer exposure durations (3 months).

It was noted earlier in this discussion that our ability to quantify adverse health effects associated with incremental sulfuric acid exposures was reasonably well-based. Such was not the case for catalyst attrition products: platinum and palladium. Scattered reports in mid-1973 from laboratories testing pre-production catalysts indicated that detectable levels of platinum and palladium were emitted as exhaust particulates. While we were able to estimate potential exposure levels, we were not able to assess the potential public health risk associated with such exposure. This was due to the fact that

extremely little had been published in the literature regarding these materials. Organic platinum compounds have, however, been identified as having adverse health effects on those occupationally exposed. As a result, an occupational TLV (threshold limit value) of 2 $\mu gm/m^3$ has been established for the work environment.

The research programs undertaken to increase our knowledge of the effects of platinum and palladium exposure cover a number of key areas:

1. Toxicology - Appendix B4 and Appendix B5
2. Inhalation Toxicology - B5
3. Human Studies - Appendix B9

These programs have presented difficult concurrent challenges. While animal exposure studies were being undertaken it became apparent that analytical methods were not really adequate to ascertain baseline or even low level concentrations in tissues and biological specimens. In addition, as noted earlier, the relevant published literature was greatly lacking -- indeed almost non-existent -- relative to any work outside of occupational exposures to organic platinum compounds.

This aspect of the catalyst program has made dramatic progress. Procedures have been designed, evaluated, and implemented for the collection and analysis of tissues and biological specimens from living human population (Appendices B9.2, B9.3, B9.4, B9.5, B9.8). Analytical techniques, an order of magnitude more sensitive than those previously available, have been developed (Appendix B4.6). The uses and sources of these metals have been documented (Appendices B9.6 and B9.7) and a broad toxicological program initiated (Appendices B4.5, B4.7, B4.8, B4.9, B4.10, B4.11, and B5.1).

To date, only acute studies have been or are nearing completion. The longer term chronic studies will not be completed until FY 77. In summary, preliminary results suggest the following:

1. Platinum, as complex salts, is a potent sensitizer and is highly allergenic.
2. We do not know what fraction of our population may be susceptible to platinum allergy.
3. Platinum and palladium can be absorbed into biological tissues when administered to experimental animals by various exposure routes.
4. Soluble platinum compounds are more toxic than lead or manganese when administered orally. Palladium is more toxic than these metals when administered intravenously.
5. Absorbed noble metals can traverse the placental barrier in pregnant experimental animals.
6. Palladium apparently acts as a non-specific cardiac irritant as well as a peripheral vasoconstrictor in experimental animals.
7. At the present time, there is relatively little, if any, contamination of platinum in human tissue.

Appendix B4.1 and Reference 16 provide an excellent, detailed overview of our current state of knowledge regarding platinum and palladium. As was evident in Table 3, presented earlier in this discussion, we do not now expect platinum or palladium exposures to be at levels of concern, based upon our current knowledge, for several years. This is principally due to the fact that all work reported by EPA's laboratories and industry laboratories indicate that platinum and palladium emissions from current production catalyst systems are below detectable limits. What emissions occur during catalyst failure due to poisoning or thermal destruction are not known, however. The potential for platinum methylation via the Vitamin B_{12} route, similar to mercury methylation, is being investigated. The status of that effort is reviewed in Appendix B4.12.

"4. Improve our understanding of the atmospheric chemistry involved and institute an appropriate air monitoring program."

Current motor vehicles emit about 1% of the total man-made SO_2 (sulfur dioxide) in the United States. This SO_2, as indeed the SO_2 from all fossil fuel combustion sources, disperses in the atmosphere and slowly reacts to form ambient airborne particulate sulfates. Some of the sulfate generated is sulfuric acid. Whether all sulfates found in the atmosphere go through the acid stage before achieving their final form is not really known. In any event, it is currently believed that the atmospheric conversion rate of SO_2 to sulfate proceeds at a rate of 2 to 4% per hour. Rates in excess of 10% per hour have been reported in the Los Angeles Basin, however.[17] Work reported by Charlson[18] suggests that the dominant sulfate species in the St. Louis Region is $(NH_4)_2SO_4$. Brosset, et al.[19] reporting on studies conducted in Sweden concluded that two types of acid particulate were present. One type, related to the phase $(NH_4)_3H(SO_4)_2$ was evidently generated by catalytic oxidation of SO_2 absorbed in water droplets about the particle. The second type, a NH_4HSO_4 phase, was very small and likely formed in the presence of NO_2. A publication by the Norwegian Ministry of Environment[20] concludes that sulfuric acid acounts for 45 to 90% of the sulfate deposited with precipitation and that long range sulfate transport accounts for a majority of such sulfates. Further, a study reported by Benarie[21] in 1972 indicated that in an urban/industrial French city sulfuric acid accounted for 7.1% of the ambient particulate sulfur, that transformation rates ranged from 6 to 25% per hour, and that no direct photochemical reactions could be recognized.

It is apparent from the foregoing that our knowledge about the atmospheric chemistry of SO_2 reactions and acid sulfates is far from complete. Several programs are under way within this particular research program and within other ORD programs to further our

knowledge in these areas. The RAPS program (Regional Air Pollution Study) in St. Louis is one such effort, which is concentrating a large number of advanced sampling stations within a defined urban area. Its objective is to describe atmospheric reaction processes and develop and validate models which could be applied to all parts of the nation. The SO_2 transformation process is one being studied in this program.

Within the catalyst program, three principal areas of investigation are being pursued. These are reviewed in some detail in Appendix B7. There areas are:

1. Smog chamber studies.
2. Sulfuric acid collection and analysis.
3. Highway studies.

The smog chamber work involves two projects. The first involves the assessment of catalyst-generated sulfuric acid aerosols' effect on visibility compared to non-catalyst vehicle exhaust effects. These studies employ a huge smog chamber (20,000 ft^3) into which the complete exhaust generated from a Federal test cycle is directed. Results are expected by February 1975 from these studies. The current status of this study is provided in Appendix B7.1. The second study involves a controlled smog chamber study aimed at ascertaining the extent of SO_2 photo-oxidation to sulfate under roadway conditions. This project is reviewed in a status report in Appendix B7.5.

Sulfuric acid is one of the oldest known irritants to man. Yet, no specific measurement method exists for the determination of sulfuric acid in ambient air. Apparently, reliable non-specific methods have been employed in Europe.[19,21] A number are currently under investigation and development in this program. Appendices B7.2, B7.3, and B7.4 review the current status of these efforts. We will likely not have a reliable measurement method for ambient sulfuric acid until FY 76.

A contract has, however, been funded for the analysis of roadside particulate by Brosset's laboratory in Sweden[19] to provide us with the benefit of their experience in this area.

The highway-related studies are reviewed in Appendices B7.6, B7.7, and B7.8 and basically involve extensive characterization of roadside aerosols in both St. Louis and Los Angeles and an assessment of SO_2 and sulfate scavenging by surfaces and materials near the roadway in Los Angeles.

Obviously, once information begins to become available from these studies we will be in a position to move from the laboratory to the real-world environment and, hopefully, gain a better grasp of the short-term reactions and transformations which could be expected to occur on and near major roadways due to SO_2 and sulfuric acid emissions from motor vehicles. Such comparative evaluations will not be possible before FY 76, however.

Quite apart from the previously discussed programs aimed at permitting estimation of exposure levels, developing SO_2 transformation mechanisms, and developing area-wide pollutant models, we are conducting two major real-world monitoring programs related specifically to the catalyst sulfate issue.

The first is a national fuel surveillance and analysis network (Appendix B1). Sulfate emissions (and also lead and other trace metal emissions) are a direct function of fuel and fuel additive composition. While the fuels used in emissions testing are related to commercially available fuels, it is virtually impossible to cover the range of such fuel and additive variations in the laboratory. This surveillance and analysis effort, therefore, provides hard data about the composition of fuels actually purchased by the consuming public. Regional shifts in fuel sulfur content, for example, would have an effect on sulfuric acid emissions from catalyst-equipped vehicles. This particular

program also supports the EPA Fuel and Fuel Additive Registration Regulations in addition to the two EPA lead in gasoline regulations.

The second monitoring program was begun in April 1974. It involves an extensive monitoring program along a Los Angeles County freeway (405) near Santa Monica. This Los Angeles site was chosen for three basic reasons:

1. Southern California gasolines typically contain much higher sulfur levels than national gasolines, thus more sulfate will be emitted by catalyst vehicles located in Southern California.
2. This freeway has a high vehicle usage: approximately 170,000 per day.
3. Meteorological conditions favored this site, i.e., the wind was predominantly perpendicular to the roadway.

This highway monitoring program is the most extensive such program conducted. It will be in operation year-round for 3 years. The objectives are three-fold:

1. to measure concentrations of motor vehicle-generated pollutants at and near the highway;
2. to measure catalyst-generated sulfuric acid at and near the highway
3. to provide input to the highway meteorological modelling program discussed earlier

The details of this program, including a review of the first 3 months data is included in Appendix B8. Appendix B8.4 specifically discusses the collection and analysis of airborne particulates near the roadway at the highway monitoring site. A special sampling device has been designed, developed, and placed on-site to permit the collection of a size fractionated ambient particulate sample of about 1 gm/day

(Appendix B8.4). Detailed trace elements (including Pt and Pd) and sulfur compound analysis will be performed on these samples. In addition, a number of prototype sampling devices are being operated at the site aimed at the collection and analysis of sulfuric acid aerosols. Some samples collected on-site have been sent to Brosset's laboratory in Sweden for acid analysis.

In support of the emissions characterization work, the statistical analysis of the data obtained for the months of June, July, and August indicate no vehicle contribution to sulfates near the roadway. Contributions to CO, total suspended particulate, SO_2, and lead are easily measurable, however.

General Discussion

This program is a complex, interdisciplinary effort involving six ORD laboratories, two ORD National Environmental Research Centers, and at least two different groups within OAWM. It should be apparent from the foregoing discussion that a high level of cooperation and interrelationships exist among the researchers and various managers involved in the program. While a large number of individual research efforts are under way which comprise this overall program, one must realize that most are in their early stages of development. It is, therefore, difficult at this point to provide clear answers to the many complex issues posed by such a difficult public health trade-off issue.

There have also been reports that catalyst-equipped vehicles emit H_2S (hydrogen sulfide), PH_3 (phosphine), partially oxygenated compounds, and perhaps even COS (carbonyl sulfide) and CS_2 (carbon disulfide). Our laboratories are investigating the possibility of emissions of these products as well. It has been suggested that one might expect the oxidation of NO/NO_2 to nitrates or nitric acid following much the same reasoning as

that associated with the generation of sulfuric acid through the oxidation of SO_2. Our laboratories, and the one industry laboratory[22] from which we have obtained data have been unable to ascertain that such products are generated across oxidation catalysts.

The catalyst issue has also stimulated our efforts to examine more fully the broader concepts encompassed by the non-regulated emissions from other engine types, such as, diesel and rotary. In addition, the Office of Air and Waste Management laboratories in Ann Arbor are sponsoring characterization programs to assess some of these non-regulated emissions from alternate sources through both the Emissions Control Technology Division and Alternative Automotive Power Systems of the Mobile Source Emissions Control Program.

The program will provide a sound technical basis for evaluating the public health issues related to both the benefits associated with regulated emissions reductions and the potential hazards associated with exposure to the sulfuric acid generated by control systems. It will also provide a sound future basis for estimating the public health impact of any mobile-source generated pollutant.

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